

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal: <https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>



Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Epitaxial monolayer CrI ₃ grown on Au(111)	Experiment number: IH-HC-3555
Beamline: ID32	Date of experiment: from: 07/10/2020 to: 13/10/2020	Date of report: 16/10/2020
Shifts:	Local contact(s): Nicholas Brookes	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Roberto Sant* : ESRF, The European Synchrotron, 38043 Grenoble France Nicholas Brookes: ESRF, The European Synchrotron, 38043 Grenoble France Kurt Kummer: ESRF, The European Synchrotron, 38043 Grenoble France Flora Yakhou Harris: ESRF, The European Synchrotron, 38043 Grenoble France		

Introduction:

CrI₃ is a layered van der Waals (vdW) material that has become an attractive research topic owing to its ferromagnetic properties both in the bulk and few-layers regime [1]. However, almost all experimental proves of few-layers CrI₃ magnetism come from exfoliated flakes, and currently only one work has been published about CrI₃ crystals prepared by epitaxial solid state methods [2]. Hereafter, we report the main results that we obtained from the preliminary characterizations of epitaxial ultra-thin films of CrI₃ grown on Au(111) substrate in our ultra-high vacuum (UHV) system.

Growth procedure:

We grew epitaxial CrI₃ by codeposition of Cr and I on Au(111) single crystal substrate using elemental Cr and a metal iodide crystal precursors. Cr atoms are deposited from an e-beam evaporator using highly pure (99.99%) Cr rods. Evaporation conditions have been found with the help of a quartz micro balance (QMB) and the effective deposited amount of material was calibrated by estimating the partial surface coverage by scanning tunnelling spectroscopy (STM). On the other hand, iodine is evaporated by applying resistive heat to a crucible containing anhydrous CrI₃ powder (99.99%). For the same reason as for CrCl₃ (see experimental report IH-MA-98), halogen atoms are preferably supplied from knudsen cells filled with metal halide compounds, e.g. CrI₃ powder in our case. We filled the crucible under inert N₂ gas atmosphere inside our glove box in order to reduce the exposure of CrI₃ to moisture, this compound being extremely hygroscopic. We evaporated CrI₃ at a temperature of 340°C, when the pressure in the chamber is steadily 8e-08mbar. We verified that this pressure is only negligibly due to source degassing and it is essentially iodine atmosphere. The codeposition time was set to reach total coverage below one monolayer and a stoichiometric ratio close to Cr:I=1:3. As opposed to CrCl₃ (see experimental report IH-MA-98), no traces of Cr were found upon evaporation of CrI₃ on the clean Au surface when the Cr source is off.

Characterization of the sample:

The as-grown sample presents a complex peculiar low energy electron diffraction (LEED) pattern that we interpreted as the superposition of the diffraction pattern from three equivalent domains of rectangular

surface cells, 60° rotated the one respect to each other (fig 1a). Our hypothesis is confirmed by the simulation in fig 1b calculated with the LEEDpat software which perfectly matches the experimental result. CrI_3 at room temperature is in fact monoclinic (90° between the two in-plane axes) and it has slightly different lattice constants close to 6.9\AA . From our simulation we deduce instead $a=7.77\text{\AA}$ and $b=14.98\text{\AA}<2a$, which points to significant lattice expansion and a distortion along one of the two planar axes. A similar picture have been observed for other monoclinic 2D crystal epitaxially grown by MBE [3].

Quantification of the deposited amount of elements has been determined by Auger electron spectroscopy (AES). We estimated from the spectrum in figure 1c a Cr:I ratio of 1:8, quite far from the expected 1:3 stoichiometry. However, the excess iodine might be in the form of elemental iodine adsorbed either on the Au surface or on the CrI_3 layer itself.

Scanning tunnelling microscopy (STM) images performed at low temperature (14K) show that the surface is widely covered by islands having long stripe shape (fig 1d-e) and an apparent height of 4\AA . Not any peculiar pattern is detectable on top of these islands and no herringbone reconstruction is visible on the free areas nearby.

X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) have been performed *in situ* on one of the samples, one day after its growth. The XAS spectra measured at the Cr $L_{2,3}$ edge show sharp features and a structured line shape, letting us deduce the material is not metallic (fig 2, top left). Moreover, the profile shape is reminiscent of the bulk case (experimental bulk CrI_3 XAS is shown in fig 2, top centre) and resembles also the one simulated by us with *Quanty*[4] using multiplet and ligand field theory (fig 2, top right). Down to 5K and with 9T magnetic field applied along the X-ray beam direction and perpendicularly to the surface, XMCD signal is 26% of the absorption (fig 2, bottom left). Also in this case, the line shape is reasonably consistent with the experimental XMCD measured from the bulk crystal (fig 2, bottom centre) – although polarized absorptions present some differences which deserve a more accurate investigation – and with our calculations as well (fig 2, bottom right). The sample is magnetically anisotropic with easy axis perpendicular to the surface plane, as expected.

Conclusions:

XAS and XMCD measurements performed so far confirm that we are able to synthesize ultra-thin CrI_3 on Au(111) by codeposition of Cr and I showing intense XMCD signal and easy axis perpendicular to the layer plane, as expected. From the synthesis point of view, a few issues remain to be solved: 1) confirm the single layer nature of the CrI_3 ; 2) identify parasitic phases and eventually get rid of them (e.g. excess iodine, CrI_2 , etc.); 3) test the effect of other substrate growth temperatures and post-growth annealing. The lack of smaller scale STM images can help to answer this question. Extended magnetic characterization is the object of a dedicated beam time that we applied for (see corresponding proposal).

References:

1. Huang et al., *Nature nanotechnology* (2018).
2. Li et al., *Science Bulletin* (2020).
3. Tsipas et al., *Advanced Functional Materials* (2018).
4. Haverkort, M., "*Quanty—a Quantum Many Body Script Language.*" (2016).

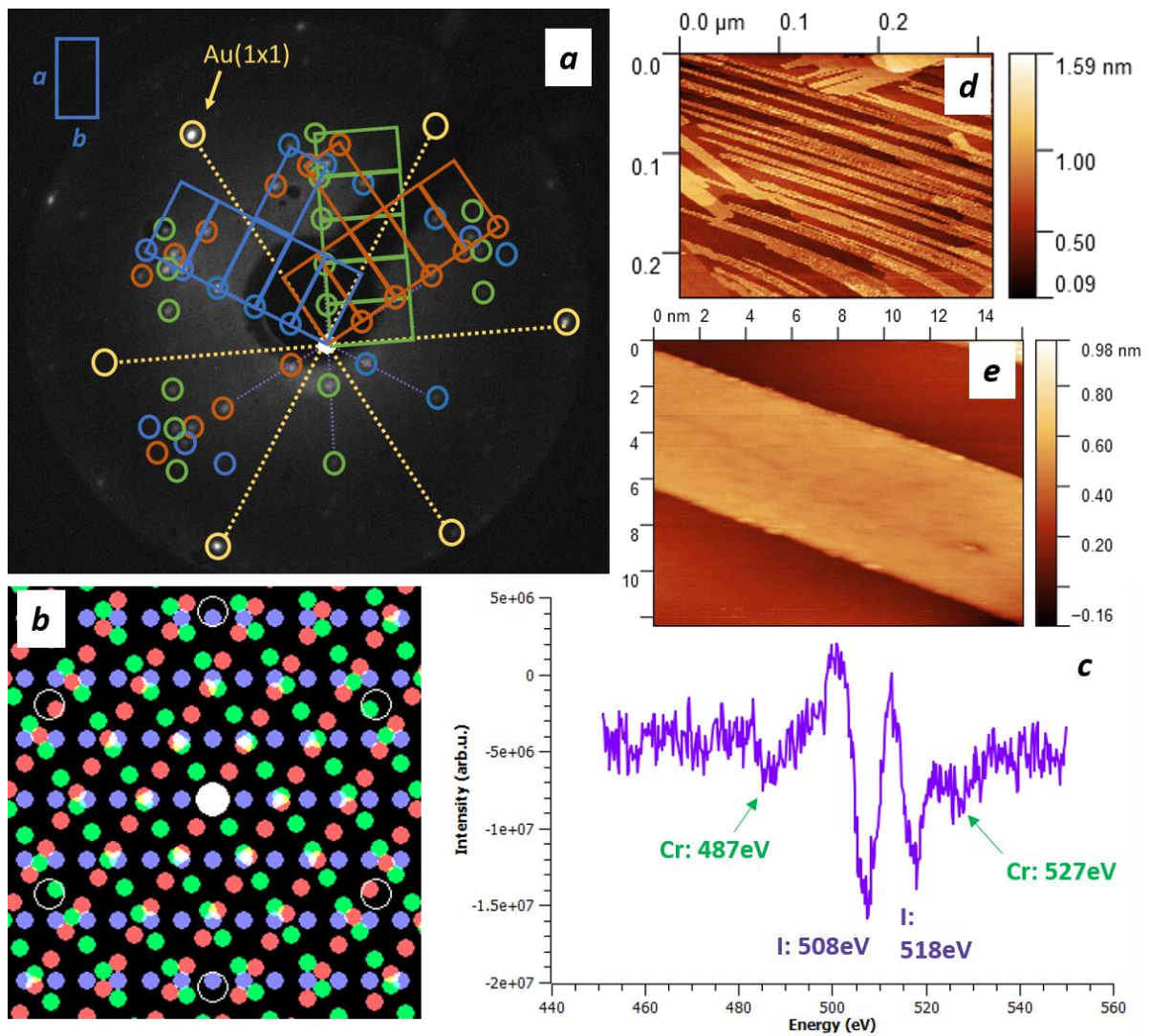


Fig1: a) LEED pattern measured at 59eV: yellow marks point to (1x1) reconstruction or substrate, while green blue and orange circles indicate reflections from 3 equivalent rectangular overlayer domains 0° , 60° , 120° rotated respectively. b) simulation of the LEED pattern in a) calculated using LEEDPat software. c) AES spectrum showing characteristic iodine and chromium peaks, from which we extracted deposited element ratio. d-e) STM images at 14K showing long narrow and straight overlayer material islands.

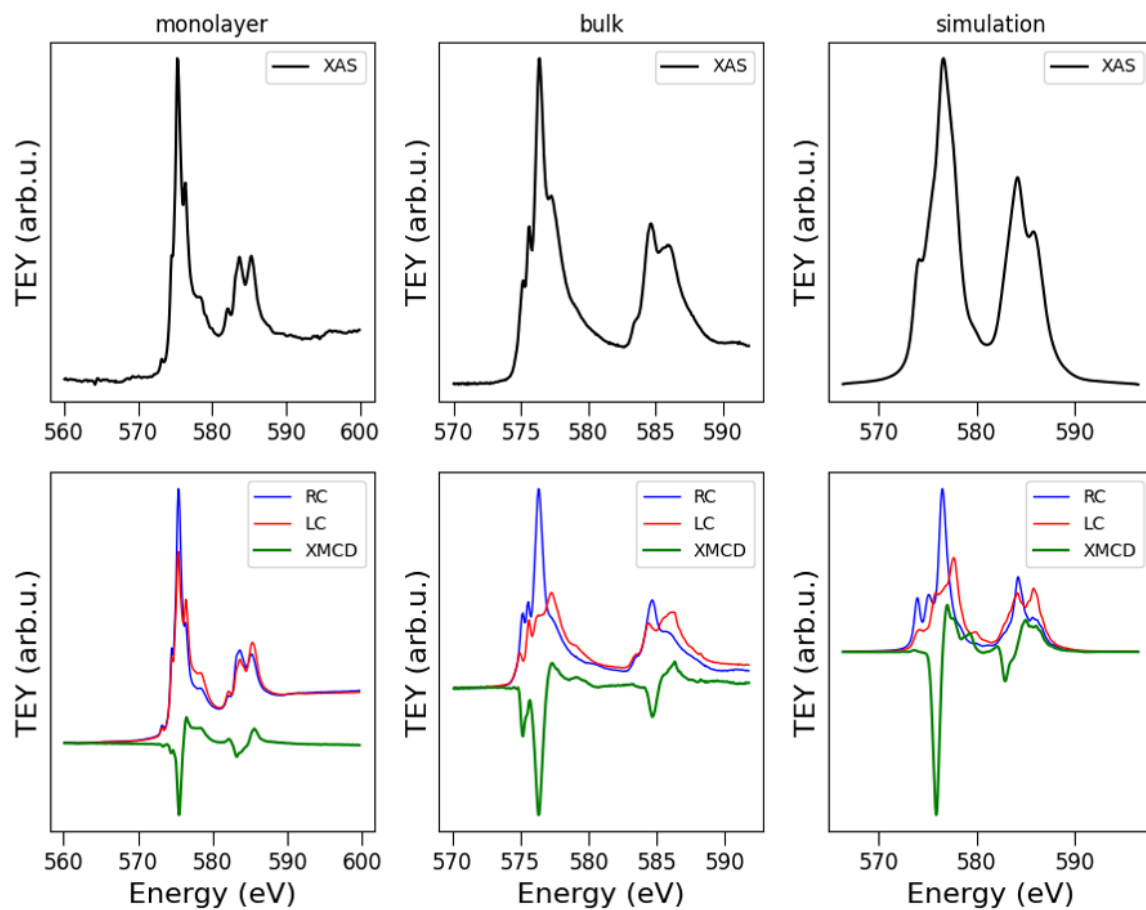


Fig2: XAS (top row) and XMCD (bottom row) spectra measured at Cr $L_{2,3}$ edge. From left to right we show experimental $\text{CrI}_3/\text{Au}(111)$, experimental bulk CrI_3 and theoretical bulk CrI_3 simulated with *Quanty*.